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(54) Title: HYDROFORMYLATION PROCESS

(57) Abstract

Process for the hydroformylation of ethylenically unsaturated compounds, by reaction with carbon monoxide and hydrogen in the presence of a catalyst based on a metal of the platinum group, a source of anions other than halide anions and a bidentate ligand of the formula $R^1R^2M^1RM^2R^3R^4$ wherein M^1 and M^2 are phosphorus, arsenic or antimony, R is a bivalent organic bridging group with 1 to 4 atoms in the bridge, R^1 and R^2 together represent a bivalent cyclic group and R^3 and R^4 independently represent an optionally substituted hydrocarbyl group or together represent a bivalent substituted or non-substituted cyclic group whereby the two free valencies are linked to M^2.

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HYDROFORMYLATION PROCESS

The invention relates to a process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst.

The hydroformylation of ethylenically unsaturated compounds to form aldehydes and/or alcohols, is of considerable industrial importance. The process has been in commercial operation for decades and over the years much development work has been done to optimize the reaction conditions, the catalyst system and the equipment. Although significant progress as regards higher yield and selectivity to the desired reaction products has been made, it is felt that in some aspects further improvement of the process is still needed.

Conventional modes of operation were initially based on the use of a cobalt carbonyl catalyst. The activity of this catalyst is relatively low and moreover, when using internal olefins as starting material, a mixture of hydroformylation products is formed containing substantial amounts of branched compounds. For many applications the presence of these branched compounds is undesirable. Moreover, in view of biological degradability, it is also considered advantageous to produce mixtures exhibiting high linear versus branching ratios.

The formation of branched products can be suppressed by using a cobalt-phosphine complex as catalyst. However at the relatively high reaction temperatures required for an adequate activity of this catalyst system, substantial amounts of saturated hydrocarbons (approximately 15%) are formed, in addition to the desired hydroformylation products.

It has been proposed to use a rhodium-based catalyst for hydroformylation reactions. A limitation of this catalyst consists in that with internal olefins as starting material, branched products are formed. In general, with a rhodium catalyst, the obtained hydroformylation product predominantly consists of aldehydes. For some

uses, e.g., for applications in the detergent industry, alcohols are a preferred starting material. Attempts have therefore been made to enhance the formation of alcohols, rather than that of aldehydes, e.g., by increasing the hydrogen versus carbon monoxide ratio, but these modes of operation invariably result in the formation of substantial amounts of saturated hydrocarbons.

It would hence be attractive if reaction conditions could be selected and a catalyst could be found such that the production of these saturated compounds is minimized.

In EP-A-0,220,767 a hydroformylation process is described, whereby an ethylenically unsaturated compound having at least 5 carbon atoms per molecule is contacted with carbon monoxide and hydrogen in the presence of an aprotic solvent and a catalyst, based on palladium, platinum or a compound of one of these metals, an anion of a carboxylic acid with a pKa of less than 2 and a bidentate of the formula $Q^1Q^2MQMQ^3Q^4$ wherein M represents phosphorus, arsenic or antimony, Q represents a divalent organic bridging group having at least three carbon atoms in the bridge and $Q^1...Q^4$ are similar or dissimilar optionally substituted hydrocarbyl groups.

From the experimental results, revealed in the examples, it can be seen that under the selected reaction conditions, the conversion is about 65%, the amount of linear compounds in the product mixture is 67% and that, although predominantly aldehydes are obtained, also some formation of paraffins takes place.

In EP-A-0,495,547 a variety of carbonylation reactions are described including the hydroformylation of ethylenically unsaturated compounds. According to one of these examples (i.e., example 27) an alpha-olefin (1-octene) may be hydroformylated at 90 °C and 60 bar (1:1) hydrogen and carbon monoxide, using a catalyst, comprising palladium, 1,3-bis(diisopropylphosphino)propane and a sulphonic acid to form 94% nonanals and 5% nonanols, the conversion being about 67%. When the same experiment is carried out at 125 °C and 60 bar (2:1) hydrogen and carbon monoxide it results in the formation of 88% nonanols and 9% nonanals with an olefin conversion of 63%. The remainder therefore comprises 1, respectively 3% paraffins. Although

suitable for the hydroformylation of alpha-olefins (initial rate of conversion in the order of about 300 mol/mol Pd.h), for the hydroformylation of internal olefins, this catalyst is found to be significantly less active (approximate rate of 25 to 30 mol/mol Pd.h).

Surprisingly, it has now been found that by selecting a catalyst based on a metal of the platinum group, a bidentate ligand comprising at least one bivalent cyclic moiety, and a source of anions other than halide anions, improved hydroformylation results are achieved as regards, inter alia, conversion rate, linearity of product and suppression of paraffin make.

Moreover, the presence of a small amount of catalyst promoter comprising a source of halide anions has been found to have a significantly favourable effect in that the hydroformylation proceeds at high rate, even at moderate temperatures, with very little formation of saturated hydrocarbons.

The invention may be defined as relating to a process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst system comprising:

a) a source of platinum group metal cations;

b) a source of anions, other than halide anions; and

c) a source of bidentate ligands of the formula

$$R^1R^2M^1RM^2R^3R^4 \qquad (I)$$

wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent organic bridging group containing from 1 to 4 atoms in the bridge, R^1 and R^2 together represent a bivalent substituted or non-substituted cyclic group whereby the two free valencies are linked to M^1 and R^3 and R^4 independently represent a substituted or non-substituted hydrocarbyl group, or together represent a bivalent substituted or non-substituted cyclic group whereby the two free valencies are linked to M^2.

Preferably, the process is carried out in the further presence of a catalyst promoter comprising a source of halide anions such that the molar ratio between halide and platinum group metal cations

is at most 3:1.

In the present specification the metals of the platinum group are defined as the metals with the atomic numbers 28, 46 and 78, i.e. nickel, palladium and platinum. Of these, palladium and platinum are preferred.

Examples of suitable metal sources are platinum or palladium compounds such as salts of palladium and nitric acid, sulphuric acid or sulphonic acids, salts of platinum or palladium and carboxylic acids with up to 12 carbon atoms, palladium- or platinum complexes, e.g. with carbon monoxide or acetylacetonate, or palladium combined with a solid material such as an ion exchanger or carbon. Palladium(II) acetate and platinum(II) acetylacetonate are examples of preferred metal sources.

As anion source, other than halide anions, any compound generating these anions may be used. Suitably, acids, or salts thereof, are used as source of anions, for example any of the acids mentioned above, which may also participate in the salts of the metals of the platinum group.

In the catalyst systems of the invention, preferably strong acids are used as anion source, i.e. acids having a pKa value of less than 3, preferably less than 2, measured in aqueous solution at 18 °C. The anions derived from these acids are non-coordinating or weakly coordinating with the metals of the platinum group.

Typical examples of suitable anions are anions of phosphoric acid, sulphuric acid, sulphonic acids and halogenated carboxylic acids such as trifluoroacetic acid.

Sulphonic acids are in particular preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-butanesulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzenesulphonic acid.

Also, complex anions are suitable, such as the anions generated by a combination of a Lewis acid such as BF_3, $AlCl_3$, SnF_2, $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$, with a protic acid, such as a sulphonic acid, e.g. CF_3SO_3H or CH_3SO_3H or a hydrohalogenic acid such as HF of HCl, or a combination of a Lewis acid with an alcohol. Examples of

such complex anions are BF_4^-, $SnCl_3^-$, $[SnCl_2.CF_3SO_3]^-$ and PF_6^-.

In bidentate ligands of formula (I), i.e., component c of the catalyst system, M^1 and M^2 are preferably the same and, more preferably, are both phosphorus atoms, in which case the ligands are bisphosphines.

In the organic bridging group, represented by R, typically all bridging groups are carbon atoms. Preferably the bridging group contains two carbon atoms in the bridge. It has been observed that the reaction rate is usually considerably enhanced, if instead of a catalyst based on a three membered bridging group, for instance a trimethylene group, a catalyst is used based on a two membered bridging group, for example an ethylene group.

This is surprising, because in earlier hydroformylation processes, such as the ones disclosed in EP-A-0,220,767 and EP-A-0,495,547, bidentate ligands are used whereby the presence of a bridging group containing 3 or more carbon atoms is preferred, or, as in EP-A-0,220,767, even required.

The bivalent (substituted) cyclic group, represented by R^1 together with R^2, in general comprises at least 5 ring atoms and preferably contains from 6 to 9 ring atoms. More preferably the cyclic group contains 8 ring atoms. Substituents, if any, are usually alkyl groups having from 1 to 4 carbon atoms. As a rule, all ring atoms are carbon atoms, but bivalent cyclic groups containing one or two heteroatoms in the ring, such as oxygen- or nitrogen, atoms are not precluded. Examples of suitable bivalent cyclic groups are 1,4-cyclohexylene, 1,4-cycloheptylene, 1,3-cycloheptylene, 1,2-cyclooctylene, 1,3-cyclooctylene, 1,4-cyclooctylene, 1,5-cyclooctylene, 2-methyl-1,5-cyclooctylene, 2,6-dimethyl-1,4-cyclooctylene and 2,6-dimethyl-1,5-cyclooctylene groups.

Preferred bivalent cyclic groups are selected from 1,4-cyclooctylene, 1,5-cyclooctylene, and methyl (di)substituted derivatives thereof.

Mixtures of ligands comprising different bivalent cyclic groups may be used as well, e.g. mixtures of ligands with 1,4-cyclooctylene and ligands with 1,5-cyclooctylene groups.

In the ligands of formula (I), R^3 and R^4 may independently represent various non-cyclic or cyclic groups, optionally substituted with substituents such as alkoxy groups with 1 to 4 carbon atoms, halogen atoms or (C_1 to C_4 alkyl)amino groups.

Examples are alkyl groups such as ethyl, isopropyl, sec-butyl and tert-butyl groups, cycloalkyl groups such as cyclopentyl and cyclohexyl groups, aryl groups such as phenyl and tolyl groups and bivalent groups such as a hexamethylene group. However, preferably R^3, together with R^4 represents a bivalent cyclic group, in particular the same group as the group represented by R^1 together with R^2, in which case the two free valencies of the bivalent cyclic group are, of course, linked to M^2, instead of M^1. Thus, preferred bidentate ligands of formula (I) are 1,2-bis(1,4-cyclooctylenephosphino)ethane, 1,2-bis(1,5-cyclooctylenephosphino)ethane and mixtures thereof.

For the preparation of the bidentate ligands, reference is made to known techniques, for example the method disclosed in GB-A-1,127,965.

The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually amounts in the range of 10^{-8} to 10^{-1}, preferably in the range of 10^{-7} to 10^{-2} mole atom of platinum group metal per mole of ethylenically unsaturated compound are used. The amounts of the participants in the catalyst system are conveniently selected such that per mole atom of platinum group metal from 0.5 to 10, preferably from 1 to 6 moles of bidentate ligand are used, from 0.5 to 15, preferably from 1 to 8 moles of anion source or a complex anion source.

A preferred feature of the process of the invention consists in the presence of a catalyst promoter, comprising a source of halide anions, with the proviso that the molar ratio between halide anions and platinum group metal cations should be at most 3:1.

If larger amounts of halide anions are present, the activity of the catalyst system is adversely affected, presumably because of co-ordination occurring between palladium and halide moieties.

Preferably, the molar ratio between halide anions and platinum

group metal cations is at most 2:1, more preferably less than 1:1, for instance from 0.02:1 to 1:1.

As source of halide anions any compound generating halide anions under the reaction conditions may be used.

Recommended are inorganic compounds such as hydrogen halides, e.g. HCl, HBr and HI and metal halides, e.g. NaCl, $MgBr_2$, $ZnCl_2$, ZnI_2, KBr, RbCl, CsCl, CsI, MgI_2 and CuCl.

Another category of recommended sources of halide anions consists of halogen containing organic compounds which are capable of providing halide anions to the reaction medium. Suitable are for example organic phosphonium halides, such as triarylalkyl phosphonium chloride and halogen containing aromatic compounds such as 5-halobenzoic acids, e.g. 5-chlorobenzoic acid, 2,5-dichlorobenzoic acid, 2,3,5-tri-iodobenzoic acid, 3,5-di-iodobenzoic acid, m-halophthalic acids and esters thereof.

Catalyst promoters comprising a source of chloride anions are in particular preferred.

The ethylenically unsaturated compound, used as starting material, is preferably an olefin having from 2 to 30 carbon atoms per molecule, or a mixture thereof. They may comprise one or more double bonds per molecule. Preferred are internal olefins having from 4 to 24 carbon atoms, or mixtures thereof. Such olefin mixtures are commercially readily available, for example the olefin mixtures, obtained as products of a process for the oligomerization of ethylene, followed by a double bond isomerization and disproportionation reaction. In the process of the invention, these internal olefins, usually mixtures of linear internal olefins with 6 to 20 carbon atoms per molecule, or closer boiling fractions of such mixtures, can be hydroformylated at high rates and an almost complete conversion. Examples are mixtures of linear internal C_6 to C_8 olefins, and of linear internal C_{10} to C_{14} olefins.

Substituted olefins may also be used, for example unsaturated carboxylic acids, esters of such acids, or unsaturated esters of carboxylic acids, e.g. allylacetate.

If desired, branched olefins such as propene trimer or isomeric

butene dimers ("DIMERSOL" a trademark) may be used, but the hydroformylation product will then, of course, contain branched structures as well.

Also, olefinically unsaturated polymeric feedstock, such as atactic polyolefins like 'Shube's' (mixture of oligomers of C_{16}-olefins), "NAPVIS" and "HYVIS" (trademarks for low molecular weight polyisobutylene) and styrene-butadiene (block)copolymers may be converted into interesting alcohols (as intermediates to synthetic lubricants, functionalized additives, etc.).

Finally, alpha-olefins, such as 1-octene and propene, and diolefins, such as norbornadiene, dicyclopentadiene, 1,5-hexadiene and 1,7-octadiene may be used. The diolefins will of course yield (predominantly) a di-hydroformylated product, although also mono-hydroformylated may be formed.

Carbon monoxide and hydrogen may be supplied in equimolar or non-equimolar ratios, e.g. in a ratio within the range of 5:1 to 1:5, typically 3:1 to 1:3. Preferably they are supplied in a ratio within the range of 2:1 to 1:2.

The hydroformylation can be suitably carried out at moderate reaction conditions. Hence temperatures in the range of 50 to 200 °C are recommended, preferred temperatures being in the range of 70 to 160 °C. Reaction pressures in the range of 5 to 100 bar are preferred, lower or higher pressures may be selected, but are not considered particularly advantageous. Moreover, higher pressures require special equipment provisions.

In the process of the invention, the ethylenically unsaturated starting material and the formed hydroformylation product may act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the hydroformylation reaction may be carried out in the additional presence of a solvent. As such, saturated hydrocarbons, e.g. paraffins and isoalkanes are recommended and furthermore alcohols, preferably having from 4 to 10 carbon atoms per molecule, such as butanol, ethylhexanol-1, nonanol-1, or in general terms the alcohols formed as hydroformylation product; ethers such as 2,5,8-trioxanonane (diglyme), diethylether and

anisole, and ketones, such as methylbutylketone.

In earlier hydroformylation processes, such as the process according to EP-A-0,495,547, the use of an alcohol as solvent was often considered undesirable, since the used hydroformylation catalysts were also catalytically active in the formation of esters in a reaction involving an olefin, carbon monoxide and the solvent alcohol. However, the catalyst systems of the present invention in view of their high selectivity towards the desired hydroformylation product, allow the use of alcohols as solvent.

It would moreover be advantageous, if the hydroformylation process could be carried out in a homogeneous reaction medium using a dissolved catalyst system of adequate activity, whereby nevertheless the catalyst, without significant loss or decomposition thereof, can be readily recovered and reused if so desired.

Accordingly, a preferred embodiment of the invention relates to a process for the hydroformylation of ethylenically unsaturated compounds having at least 4 carbon atoms by reaction thereof with carbon monoxide and hydrogen in a single-phase liquid medium, in the presence of the aforementioned catalyst system, followed by effecting the formation of a multiphase liquid reaction medium comprising one phase in which substantially all platinum group metal cations of the catalyst system is present and at least one further phase containing a major portion of the hydroformylated product.

The unsaturated compounds used in the process of this embodiment contain at least 4 carbon atoms per molecule. It has been established that with ethylenically unsaturated compounds having only 2 or 3 carbon atoms per molecule, the formation of a multi-phase liquid reaction medium, whereby the platinum group metal cations of the catalyst system is present in one phase and a major portion of the formed hydroformylated product in another phase, can not be easily effected. Preferably, ethylenically unsaturated compounds are used, having at least 6 carbon atoms per molecule.

In particular preferred are ethylenically unsaturated compounds having from 6 to 22 carbon atoms per molecule. A preferred starting material consists of internal linear olefins having from 12 to 16

carbon atoms per molecule.

The formation of the multiphase liquid reaction medium, following the hydroformylation reaction, can be effected in various ways.

For example, a selective solvent for the hydroformylated product may be added to the single-phase liquid reaction mixture, during or subsequent to the hydroformylation reaction, forming a second liquid phase in which a major portion of the hydroformylated product(s), and possibly part of any unconverted unsaturated starting material will be found.

Whereas in this embodiment two liquid phases are formed allowing an adequate separation between the catalyst system on the one hand and a major portion of the hydroformylation product on the other hand, it will be necessary to remove the hydroformylated product from the said second liquid phase, containing the added solvent.

Therefore, it is preferred to effect the formation of a multiphase liquid reaction medium by adding to the single-phase liquid reaction medium during or subsequent to the hydroformylation reaction, an inert solvent, capable of selectively dissolving substantially all platinum group metal of the catalyst system. This embodiment allows an adequate separation between the hydroformylated product and the catalyst system, at the same time simplifying the recovery of the hydroformylated product.

According to a still more preferred embodiment, the hydroformylation reaction is carried out in the presence of an inert solvent and, subsequent to the reaction, the multiphase liquid reaction medium is formed by cooling the reaction medium, obtained in the reaction.

In this manner it is possible to ensure, that substantially all platinum group metal of the catalyst system, i.e. at least 95% and in particular at least 97% of the platinum group metal, is present in the liquid phase, containing the inert solvent.

A major portion of the hydroformylated product, i.e. at least 50% and in particular at least 80% of the hydroformylated product is obtained in another liquid phase, from which it can be easily recovered by known techniques.

By selection of a suitable solvent the multiphase liquid medium is readily formed when the temperature of the reaction mixture is decreased to ambient temperatures. If desired, the reaction medium can be cooled to lower temperatures, but for large-scale operation this is not considered of special advantage, in view of the additional provisions to be made in the reactor section of the equipment.

Suitable inert solvents, , which may be added instead of, or in addition to the solvents mentioned above, that are capable of selectively dissolving substantially all platinum group metal of the catalyst system, are usually characterized by the presence of an aprotic, polar group in the molecule.

Solvents containing strong polar groups are in particular preferred if the unsaturated starting material has a relatively low molecular weight, i.e., if ethylenically unsaturated compounds having from 5 to 7 carbon atoms are used.

For the hydroformylation of higher molecular weight unsaturated compounds, e.g. olefins having from 12 to 16 carbon atoms the use of less polar inert solvents will usually be satisfactory.

Solvents, comprising or substantially consisting of sulphones are preferred. Sulphones are in particular preferred, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide), sulfolene, 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

Sulfolane has proved to be a most effective solvent for the formation of a multiphase liquid reaction medium.

It has been found particularly beneficial to carry out the invention using sulfolane as solvent and a catalyst system based on a complex anion (for instance based on $SnCl_2$) and/or in the presence of a catalyst promoter, to counter the somewhat increased paraffin formation due to presence of the solvent.

Mixtures of solvents may also be used, for example a mixture of a sulphone with a protic solvent, such as an alcohol. In the hydroformylation of olefins, typically an alcohol is selected which is identical or similar to an alcohol as obtained in the hydroformyla-

tion reaction.

The amount of solvent to be used in the process of the invention may vary considerably. It is within the reach of those skilled in the art to establish in each case the degree of cooling and the optimal amount of solvent required for the formation of a multiphase liquid reaction medium. The experimental results provided hereinafter, are also indicative for the amount of solvent, preferably to be used.

The process of the invention is eminently suitable to be used for the preparation of alcohols from internal olefins at high rate, in particular by using a catalyst system as defined above, based on palladium as platinum group metal.

Furthermore the process is very useful for the preparation of aldehydes having a high linearity, in particular by using a catalyst system as defined above, based on platinum as platinum group metal.

The invention will be illustrated by the non-limiting examples, as described hereinafter. The abbreviations, used in the Tables have the following meanings:

BCPE = 1,2-bis(1,4-cyclooctylenephosphino)ethane
BCPP = 1,3-bis(1,4-cyclooctylenephosphino)propane
BBPE = 1,2-bis(sec-butylphosphino)ethane
BBPP = 1,3-bis(sec-butylphosphino)propane
BDPE = 1,2-bis(2,6-dimethyl-1,4-cyclooctylenephosphino)ethane
BCPI = 1,2-bis(1,4-cyclooctylenephosphino)propane
MSA = methanesulphonic acid
TFSA = trifluoromethanesulphonic acid
TMSA = 2,4,6-trimethylbenzenesulphonic acid
t-BSA = tert-butanesulphonic acid
EH = 2-ethylhexan-1-ol
HBF_4 = fluoboric acid

Examples 1 - 2

The experiments were carried out in a 250 ml magnetically stirred autoclave. The autoclave was charged with 20 ml of 1-octene, 20 ml 2,5,8-trioxanonane (diglyme), 0.25 mmol of palladium(II) acetate, 0.6 mmol of bisphosphine ligand and 1 mmol of MSA. After being

flushed, the autoclave was pressurized with carbon monoxide and hydrogen to a partial pressure of 30 bar of each. Subsequently, the reactor was sealed and the contents were heated to the pre-set temperature and maintained at that temperature until the reaction was substantially complete. After cooling, a sample was taken from the contents of the reactor and analysed by Gas Liquid Chromatography. Further details and the results of the analysis can be found in Table I.

The calculated conversion rate is expressed as moles of product per mole atom of platinum group metal and per hour, (mol/mol.h).

The amount of produced paraffins was less than 1%. Comparison of Examples 1 and 2 with Example 27a of EP-A-0,495,547 reveals that in contrast to use of 1,3-bis(diisopropylphosphino)propane, use of the BCPE affords the alcohol product rather than the aldehyde.

Example 3

The experiment was performed substantially according to the procedure as described for Examples 1-2. The autoclave was charged with a partial pressure of 20 bar of ethene, carbon monoxide and hydrogen each, 45 ml of diglyme, 0.25 mmol of palladium(II) acetate, 0.6 mmol of BCPE and 0.4 mmol of $SnCl_2$ and TFSA each. At 100 °C, ethene was converted into propanal (selectivity >98%) at a rate of 2,000 mol/mol.h.

Example 4

The experiment was performed substantially according to the procedure as described for Example 3. The autoclave was charged with a partial pressure of 10 bar of ethene, 20 bar of carbon monoxide and 40 bar of hydrogen, 45 ml of diglyme, 0.25 mmol of palladium(II) acetate, 0.3 mmol of BCPE, 0.4 mmol of TMSA and 0.1 mmol of HCl. At 105 °C, ethene was converted into propanol (selectivity >98%) at a rate of 1,000 mol/mol.h.

Examples 5 - 9 and Comparative examples A and B

The experiments were performed substantially according to the procedure as described for Examples 1-2. The autoclave was charged with 30 ml of internal olefins with 14 carbon atoms ("i-$C_{14}^{=}$"), 50 ml of a solvent, 0.25 mmol of palladium(II) acetate, 0.6 mmol of

bisphosphine ligand and a specified amount of an acid catalyst component. Further details and the analytical results are provided in Table II.

The amount of produced paraffins was less than 1%.

By comparing the results of Examples 5 and 7, it can be seen, that by using a ligand comprising a bridging moiety with two atoms in the bridge a higher conversion rate at a lower temperature is achieved whereby more linear hydroformylation products are formed, than by using a ligand comprising a 3-membered bridging element.

The effect of using different acid catalyst components can be seen by comparing the results of Examples 8 and 9.

The results of comparative example A show, that by using a ligand, outside the scope of the invention, even at a relatively high temperature, predominantly aldehydes are formed of poor linearity and at low rate. Moreover, in the experiment of Comparative example B, again using a ligand outside the scope of the invention, it is shown that the use of that ligand prevents the use of an alcohol as solvent as instead of the desired product a considerable amount of ester is formed.

Example 10

A 250 ml autoclave, magnetically stirred, was charged with 37.5 ml (148 mmol) of i-$C_{14}^{=}$, 0.312 mmol of palladium(II) acetate, 0.625 mmol of BCPE, 0.625 mmol of TFSA, 0.625 mmol of tin chloride ($SnCl_2$), 0.52 gram of water, 52.5 ml of EH and 10 ml of sulfolane.

After being flushed, the autoclave was pressurized with a hydrogen and carbon monoxide mixture in a molar ratio of 2:1, up to a total pressure of 90 bar. Subsequently, the autoclave was sealed and the contents were heated to 105 °C.

After a reaction period of 4 hours, during which no further hydrogen or carbon monoxide was supplied, the single-phase reaction mixture was cooled to ambient temperature, whereby two liquid layers were formed.

From each of the two layers, (product and sulfolane layer) a sample was taken and analysed by GLC.

The conversion, selectivities and analytical results are given

below.

i-$C_{14}^{=}$ conversion (after 2 hours) (% of feed)	90.0
id. at the end of the reaction (4 hours)	98.4
C_{15} alcohols formed (% of GLC-area)	97.4
C_{15} aldehydes formed (% of GLC-area)	1.0
C_{14} paraffins formed (% weight of olefins)	0.4
Linearity C_{15} alcohols (%)	69.9
Palladium concentration in product layer (ppm)	9.1 (+/- 0.4)
id. in sulfolane layer (ppm)	3320 (+/- 160)

Example 11

An experiment was carried out, substantially as described in Example 10, with the following differences:

i) the amount of $SnCl_2$ was 0.15 mmol, instead of 0.625 mmol;

ii) the amount of water was 0.5 g, instead of 0.52 g and

iii) the total pressure was 50 bar and was maintained at that value during the reaction.

The conversion, selectivities and analytical results are set out below:

i-$C_{14}^{=}$ conversion (after 2 hours) (% of feed)	85.8
id. at the end of the reaction (6 hours)	99.5
C_{15} alcohols formed (% of GLC-area)	97.7
C_{15} aldehydes formed (% of GLC-area)	0.8
C_{14} paraffins formed (% weight of olefins)	0.7
Linearity C_{15} alcohols (%)	70.4
Palladium concentration in product layer (ppm)	14.3 (+/- 0.7)
id. in sulfolane layer (ppm)	3850 (+/- 190)

Example 12

An experiment was carried out, substantially as described in Example 11, with the difference that 0.625 mmol of $SnCl_2$, instead of 0.15 mmol was added.

The conversion, selectivities and analytical results are given below.

$i\text{-}C_{14}^{=}$ conversion (after 2 hours) (% of feed)	72.2
id. at the end of the reaction (6 hours)	97.5
C_{15} alcohols formed (% of GLC-area)	96.9
C_{15} aldehydes formed (% of GLC-area)	1.0
C_{14} paraffins formed (% weight of olefins)	0.5
Linearity C_{15} alcohols (%)	71
Palladium concentration in product layer (ppm)	10.3 (+/- 0.5)
id. in sulfolane layer (ppm)	3465 (+/- 170)

The weight ratio between the product layer and the sulfolane layer was typically 88% : 12%. The sulfolane layer typically contained 83% w of sulfolane and 17% w of EH.

Examples 13 - 26

The experiments were carried out in a 350 ml "HASTELLOY C" (HASTELLOY is a trademark) magnetically stirred autoclave.

The autoclave was charged with 30 ml of $i\text{-}C_{14}^{=}$, 25 ml (or 45 ml) of EH, 6 ml of sulfolane, 0.25 mmol of palladium(II) acetate, 0.6 mmol of BCPE, 0.5 mmol of TFSA and a catalyst promoter.

After being flushed, the autoclave was pressurized with a 1:2 molar mixture of carbon monoxide and hydrogen up to a pressure of 60 bar and subsequently sealed. The temperature of the mixture was raised to the pre-set value.

After a reaction period of 3-10 hours, the reaction was discontinued and the reaction mixture cooled to ambient temperature.

A sample was taken from the contents of the reactor and analysed by GLC. The $i\text{-}C_{14}^{=}$ conversion was > 99%; further details and analytical results are compiled in Table III. From this table it can be seen that the addition of a catalyst promoter is very beneficial in respect of the reduction of paraffin formation (cf. Examples 28-31 hereinafter).

Example 27

An experiment was carried out, substantially as described with respect to Examples 13-26, with the difference that 45 ml of EH and, instead of BCPE, 0.6 mmol of BDPE was used.

The $i\text{-}C_{14}^{=}$ conversion was > 99%. Further details and results are

included in Table III.

Example 28

An experiment was carried out, substantially as described with respect to Examples 13-26, with the difference that no catalyst promoter was applied. The results are included in Table III to highllight the preference for the copresence of a catalyst promoter.

Example 29

An experiment was carried out, substantially as described with respect to Examples 13-26, with the difference that instead of a catalyst promoter, 0.3 mmol of t-BSA was added. From the results, as given in Table III, it can be seen that the rate of the reaction is increased. Nonetheless, the production of paraffins is higher than in the experiments carried out in the presence of a catalyst promoter.

Example 30

An experiment was carried out, substantially as described with respect to Examples 24 and 25, with the differences that the reaction temperature was 99 °C and that instead of 2,5-dichlorobenzoic acid, 5 mmol of 2,6-dichlorobenzoic acid was used as catalyst promoter. From the results, as given in Table III, it can be seen that by using an o,o-dihalo compound which will less easily generate halide anions, the reaction rate is increased, but that the paraffin production is not below 1%.

Example 31

An experiment was carried out, substantially as described with respect to Examples 24 and 25, with the difference that instead of 2,5-dichlorobenzoic acid, 5 mmol of 2,5-dihydroxybenzoic acid was used as catalyst promoter. From the results, as given in Table III, it can be seen that by using a promoter which is not capable of generating halide anions, the additional improvement achieved in the co-presence of a catalyst promoter as regards reaction rate and paraffin production is not achieved.

Example 32

The experiment was performed substantially according to the procedure as described for Examples 1-2. The autoclave was charged

with 20 ml of isomeric butene dimers ("DIMERSOL"), 50 ml of a solvent, 0.25 mmol of palladium(II) acetate, 0.6 mmol of bisphosphine ligand and a specified amount of an acid catalyst component. Further details and the analytical results are provided in Table IV.

The amount of produced paraffins was less than 1%.

Examples 33 - 39

The experiments were performed substantially as described in Example 32.

The autoclave was charged with 20 ml of a branched olefin (either "DIMERSOL", propylene trimer = PT-3 or diisobutylene), 0.25 mmol of palladium(II) acetate, 0.6 mmol of bisphosphine ligand, a specified amount of an acid catalyst component, a specified amount of a solvent and a specified amount of catalyst promoter. Further details and results are provided in Table IV.

Examples 40 - 47

The experiments were performed, substantially as described above for Examples 1-2.

The autoclave was charged with 20 ml of 1-octene, 40 ml of diglyme, 0.25 mmol of platinum(II) acetylacetonate, 0.6 mmol of bisphosphine ligand and a specified amount of an acid catalyst component and/or other anion source. Further details and results are provided in Table V.

Comparing the results of Examples 44 and 45 with those of Example 43 shows that the addition of acid (acetic acid) results in an increase in rate of conversion.

Example 48 - 50

The experiment was performed substantially as described in Examples 40-47.

The autoclave was charged with 20 ml of 1-octene, 40 ml of diglyme, 0.25 mmol of platinum(II) acetylacetonate, 0.3 mmol of bisphosphine ligand, a specified amount of an acid catalyst component and (for Example 51) a specified amount of a catalyst promoter. Further details and results are provided in Table V.

Examples 51 - 54

The experiments were performed substantially as described in

Examples 40-47 with the difference that 20 ml of propene was supplied, instead of 1-octene. Examples 53 and 54 where carried out using 0.3 instead of 0.6 mmol of bisphosphine ligand.

The selectivity to butanals was >98%. Further details and results are provided in Table VI.

Example 55

The experiments were performed substantially as described in Examples 53 and 54, using a slightly different catalyst system and a carbon oxide to hydrogen molar ratio of 1:2. Further details and results are provided in Table VI.

Examples 56 - 57

The experiments were performed substantially as described in Examples 51-52.

The autoclave was charged with 20 ml of propene, 50 ml of octanol, 0.25 mmol of palladium(II) acetate, 0.6 mmol of bisphosphine ligand and a specified amount of catalyst promoter. Further details and results are provided in Table VI.

Examples 58 - 62

The experiments were performed, substantially as described in Examples 51 and 52, using different olefins and substituted olefins, instead of propene.

In all experiments the anion source was 0.5 mmol of TFSA and 0.5 mmol of $SnCl_2$. Further details and results are provided in Table VII.

Examples 63 - 65

The experiments were performed, substantially as described in Examples 59 and 60. In all experiments, the initial rate (addition of the first methylol group) was found to be very high (e.g., in 0.5 hour dicyclopentadiene was converted for 100% into one of its monoalcohols, 8- respectively 9-methylol-tricyclo[5,2,1,$0^{2,6}$]dec-3-ene), whereas addition of the second methylol group required more time (about 10 hours). Further details and results are provided in Table VII.

Table I (Pd-based catalyst system)

Example No	Ligand	Anion source (mmol)	Temp. (°C)	Rate (mol/mol.h)	Product(s) Selectivity (%)	Linear (%)
1	BCPE	MSA (1)	125	250	nonanol (98)	67
2	BCPE	MSA (1)	100	200	nonanol (98)	64

Table II (Pd-based catalyst system)

Example No	Ligand	Anion source (mmol)	Solvent	Temp. (°C)	Rate (mol/mol.h)	Product(s) Selectivity (%)	Linear (%)
5	BCPE	TFSA (1)	EH	88	100	C_{15}-alcohol (>98)	62
6	BCPE	HBF_4 (1)	EH	115	200	C_{15}-alcohol (>98)	70
7	BCPP	TFSA (1)	1-octanol	120	30	C_{15}-alcohol (>98)	53
8	BCPE	TFSA (1)	anisole	90	200	C_{15}-alcohol (>98)	78
9	BCPE	t-BSA (0.5)	anisole	88	100	C_{15}-alcohol (>98)	47
A	BBPE	TFSA (0.5)	diglyme	125	< 10	C_{15}-alcohols (15)	45
						C_{15}-aldehydes (85)	45
B	BBPP	MSA (0.5)	EH	145	20	C_{15}-alcohol (70)	50
						2-EH ester of C_{15}-alkanoic acid (30)	

Table III (Pd-based catalyst system)

Example No	Promoter (mmol)	Temp. (°C)	Rate (mol/mol.h)	Linearity (%) C_{15}-alcohols	Paraffins production (%)
28	-	96	125	70.9	2.5
13	HCl (0.1)	96	450	72	0.2
14	HCl (0.05)	98	500	71	0.8
15	HCl (0.1)	98	450	71	0.5
16	HBr (0.1)	96	400	71.8	0.3
17	HI (0.1)	100	200	75	0.7
29	t-BSA (0.3)	98	300	70.3	2.5
18	NaCl (0.1)	98	275	69.5	0.4
19	NaCl (0.25)	95	450	65.8	0.3
20	$MgBr_2.6H_2O$ (0.1)	99	200	68	0.5
21	$ZnCl_2$ (0.13)	118	450	70.7	1.2
22	ZnI_2 (0.1)	99	350	73.6	0.5
23	triphenylmethylphosphoniumchloride (0.1)	96	350	69.7	0.3
24	2,5-dichlorobenzoic acid (5) + 45 ml EH	96	375	70.6	0.4
25	2,5-dichlorobenzoic acid (2) + 45 ml EH	95	360	70	0.3
30	2,6-dichlorobenzoic acid (5) + 45 ml EH	99	300	70.8	1.2
31	2,5-dihydroxybenzoic acid (5) + 45 ml EH	95	125	70	2.2
26	2,3,5-trichlorobenzoic acid (0.1)	99	250	76.7	0.8
27	$ZnCl_2$ (0.12) + 45 ml EH	100	150	74.2	1.0

Table IV (Pd-based catalyst system)

Example No	Ligand	Anion source (mmol)	Promoter (mmol)	Solvent (ml)	Temp. (°C)	Conversion (%)	Product(s)
32	BCPE	MSA (0.5)	-	EH	110	95 after 20h	C_9-"DIMERSOL" alcohols
33	BCPP	TFSA (0.5)	HCl (0.1)	EH (40)	100	94 after 3 h	ibid
34	BCPP	TFSA (0.5)	HCl (0.1)	EH (25) sulfolane (6)	100	88 after 3 h	ibid
35	BCPE	H_2SO_4 (0.5)	HCl (0.1)	EH (35) sulfolane (6)	100	92 after 2h	ibid
36	BCPP	MSA (1)	HCl (0.1)	EH (40) sulfolane (10)	135	82 after 5h	ibid
37	BCPE	TFSA (0.5)	HCl (0.1)	EH (40) sulfolane (10)	135	73 after 8h	C_{10}-alcohols
38	BCPE	TFSA (0.5)	HCl (0.1)	EH (40) sulfolane (10)	145	75 after 5h	ibid
39	BCPE	TFSA (0.5)	HCl (0.1)	EH (25) sulfolane (6)	96	95 after 2h	C_9-diisobutylene alcohol

Table V (Pt-based catalyst system)

Example No	Ligand	Anion source (mmol)	Temp. (°C)	Rate (mol/mol.h)	Product(s) Selectivity (%)	Linear (%)
40	BCPE	t-BSA (1)	137	50	nonanol (> 98)	91
41	BCPE	TFSA (1)	128	100	nonanal (~ 12)	88
					nonanol (~ 86)	
42	BCPE	$SnCl_2$ (1)	125	70	nonanal (> 98)	98
43	BCPE	TFSA (0.5)	88	150	nonanal (> 98)	98
		$SnCl_2$ (0.5)				
44	BCPE	TFSA* (0.5)	75	300	nonanal (> 98)	98
		$SnCl_2$ (0.5)				
45	BCPE	TFSA* (0.5)	90	500	nonanal (> 98)	98
		$SnCl_2$ (0.5)				
46	BCPE	TFSA (0.5)	80	100	nonanal (> 98)	99.3
		$SnCl_2$ (0.5)				
47	BCPI	TFSA (0.5)	80	150	nonanal (> 98)	98.6
		$SnCl_2$ (0.5)				
48	BCPE	TMSA (0.4)	80	120	nonanal (> 98)	96
49	BCPE	t-BSA (0.4)	80	100	nonanal (> 98)	94
50	BCPE	TMSA (0.4)	80	150	nonanal (> 98)	96
		HCl (0.1)				

* 5 ml of acetic acid was added.

Table VI (Pt-* or Pd-based catalyst system)

Example No	Ligand	Anion source (mmol)	Promoter (mmol)	Temp. (°C)	Rate (mol/mol.h)	Product(s) Selectivity (%)	Linear (%)
51*	BCPP	MSA (0.5) $SnCl_2$ (0.5)	-	118	200	butanal (>98)	83
52*	BCPE	TFSA (0.5) $SnCl_2$ (0.5)	-	102	550	butanal (>98)	94
53*	BCPE (0.3)	$SnCl_2$ (0.4)	HCl (0.4)	95	300	butanal (>98)	95
54*	BDPE (0.3)	$SnCl_2$ (0.4)	HCl (0.4)	95	100	butanal (>98)	97
55*	BDPE (0.3)	TMSA ((0.4)	HCl (0.1)	105	300	butanol (95)	93
56	BCPE	TFSA (0.5)	HI (0.2)	115	4,100	butanol (92)	78
57	BCPE	TFSA (0.5)	HCl (0.2)	115	5,600	butanol (93)	73

Table VII (Pt-based catalyst system)

Example No	Reactant	Ligand	Anion source (mmol)	Promoter (mmol)	Temp. (°C)	Rate (mol/mol.h)	Product(s) Selectivity (%)	Linear (%)
58	ethene	BCPE	MSA (0.5) $SnCl_2$ (0.5)	-	90	1,500	C_3-aldehyde (98)	
59	1,5-hexadiene	BCPE	MSA (0.5) $SnCl_2$ (0.5)	-	92	300	octanedial (98)	92
60	norbornadiene	BCPE	MSA (0.5) $SnCl_2$ (0.5)	-	92	750	norbornane dialdehyde (98)	
61	allylacetate	BCPE	MSA (0.5) $SnCl_2$ (0.5)	-	75	150	4-acetyloxy-butanal (98)	95
62	4-pentenoic acid	BCPE	MSA (0.5) $SnCl_2$ (0.5)	-	80	200	5-carboxypentanal (98)	95
63	1,5-hexadiene	BCPE (0.3)	TMSA (0.4)	HCl (0.1)	100	150	1,8-octanediol (98)	90
64	norbornadiene	BCPE (0.3)	TMSA (0.5)	HCl (0.1)	100	400	dimethylol norbornane (98)	
65	dicyclopentadiene	BCPE (0.3)	TMSA (0.5)	HCl (0.1)	100	800	dimethylol dcpd (98)	67

C L A I M S

1. A process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst system comprising:

a) a source of platinum group metal cations;

b) a source of anions, other than halide anions; and

c) a source of bidentate ligands of the formula

$R^1R^2M^1RM^2R^3R^4$ (I)

wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent organic bridging group containing from 1 to 4 atoms in the bridge, R^1 and R^2 together represent a bivalent substituted or non-substituted cyclic group whereby the two free valencies are linked to M^1 and R^3 and R^4 independently represent a substituted or non-substituted hydrocarbyl group, or together represent a bivalent substituted or non-substituted cyclic group whereby the two free valencies are linked to M^2.

2. A process as claimed in claim 1, carried out in the further presence of a catalyst promoter comprising a source of halide anions such that the molar ratio between halide and platinum group metal cations is at most 3:1.

3. A process as claimed in claim 2, wherein the molar ratio between halide and platinum group metal cations is in the range from 0.02:1 to 1:1.

4. A process as claimed in any one of claims 1 to 3, wherein the catalyst system is based on a palladium or platinum compound.

5. A process as claimed in any one of claims 1 to 4, wherein the catalyst system is based on a source of bidentate ligands of formula (I), wherein M^1 and M^2 each represent a phosphorus atom.

6. A process as claimed in any one of claims 1 to 5, wherein in the bidentate ligand of formula (I) R represents an ethylene group.

7. A process as claimed in any one of claims 1 to 6, wherein in the bidentate ligand of formula (I) the bivalent cyclic group, represented by R^1 together with R^2, is a cycloalkylene group having from 6 to 9 ring atoms, preferably 8 ring atoms.

8. A process as claimed in any one of claims 1 to 7, wherein in the bidentate ligand of formula (I) R^3 together with R^4, has the same meaning as R^1 together with R^2, whereby the two free valencies are linked to M^2.

9. A process as claimed in any one of claims 1 to 8, for the hydroformylation of ethylenically unsaturated compounds having at least 4 carbon atoms by reaction thereof in a single phase liquid medium, followed by effecting the formation of a multiphase liquid reaction medium comprising one phase in which substantially all platinum group metal cations is present and at least one further phase containing a major portion of the hydroformylated product.

10. A process as claimed in claim 9, wherein the formation of the multiphase liquid reaction medium is effected with the aid of an inert solvent capable of selectively dissolving substantially all platinum group metal cations from a single phase liquid medium containing dissolved platinum group metal cations and hydroformylated product, such as sulfolane, an alkyl- or dialkylsulfolane, by cooling the reaction medium subsequent to the reaction.

INTERNATIONAL SEARCH REPORT

Internat Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C29/16 C07C31/12 C07C31/125 C07C31/27 C07C45/50
C07C47/02 C07C47/12 C07C47/133 C07C51/373 C07C67/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 529 698 (SHELL INTERNATIONALE RESEARCH) 3 March 1993 see the whole document see example 7	1,4-9
X	EP,A,0 495 547 (SHELL INTERNATIONALE RESEARCH) 22 July 1992 cited in the application see the whole document	1,4-10
A	EP,A,0 220 767 (SHELL INTERNATIONALE RESEARCH) 6 May 1987 cited in the application see the whole document	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
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